# OPTICAL PROPERTIES OF SUBLIMED 2,4,6-TRINITROTOLUENE

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## THESIS

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Lieutenant Commander, United States Navy

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ABSTRACT

Investigation of the literature indicates conflicting conclusions on the crystallographic system of 2,4,6-Trinitrotoluene. This study determined the optical properties of TNT crystallized a few degrees from its melting point by a sublimation technique. The crystal is classified as monoclinic from evidence of horizontal dispersion in thin sections. Refractive indices determined by the Becke line method under sodium D light and corrected to 25° C. are: $N_x$ 1.544 ± 0.002, $N_y$ 1.671 ± 0.002, $N_z$ 1.725 ± 0.005. Optical character is biaxial with a negative sign of double refraction. Dispersion is greater for light of red wave lengths than for light of violet wave lengths. The optic angle, 2V, is 61.92°. The apparent optic angle, 2E, is 118.58°.

It is plausible to suspect that crystalline imperfections contribute to the inherent instability of explosive materials. No striking irregularities attributable to imperfections are noted in conventional optic interference figures. Additionally, no evidence of twinning was observed.

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1. Introduction.

Explosives are by nature highly unstable materials. The exact cause of this instability is imperfectly understood. It is known, however, that imperfections in crystalline substances are capable of releasing energy under certain circumstances. Therefore, it is plausible to suspect that such imperfections, if of sufficient magnitude, might contribute materially to their inherent instability. Before this suspicion can be confirmed, however, considerable basic research is required to establish the correct physical properties and structural features of many of the explosive crystals. Chemical details in general are well known. Crystallographic data, on the other hand, are sketchy and contradictory (Reference 1).

Investigation of the literature reveals conflicting conclusions on the crystal system of TNT (2,4,6-Trinitrotoluene). Friedlander (year 1879, Reference 2) reported the crystal system orthorhombic. Artini (1915, Reference 3) and Hertel and Romer (1930, Reference 4) reported the crystal as monoclinic. Hultgren (1936, Reference 5) and McCrone (1949, Reference 6) reported the crystal orthorhombic. Ito (1950, Reference 7) reported the crystal with one orthorhombic and two monoclinic forms. Investigators of the Karpov Physical Chemistry Institute of Moscow (1953, Reference 8) concluded that no true monoclinic form exists. Burkhardt and Bryden (1953, Reference 9) reported four monoclinic and three orthorhombic forms of TNT The work of Ito and Burkhardt and Bryden indicated the polymorphism of TNT in the same batch of crystals

obtained from a solution medium. Burkhardt and Bryden succeeded consistently in procuring crystals reported as monoclinic by a sublimation technique. The only optical investigations indicated in the literature were conducted by McCrone who obtained orthorhombic crystals from solutions of ethanol and acetone.

Since the optical properties of the sublimed TNT, reported as monoclinic from X-ray analysis (Reference 9), had not been classified, this material was selected for study. The purpose of this work is to obtain and compare the optical properties of the sublimed form of TNT with the existing data on the orthorhombic form. Additionally, it is desired to investigate the suitability of the techniques of optical crystallography to indicate the presence of crystalline imperfections.

2. General Discussion.

Crystalline substances possess unique optical properties. Optical Crystallography is the means of classifying such properties for non-opaque crystals. Its theory explains the phenomena observed under the petrographic microscope. Its techniques permit determining the principle indices of refraction, the crystallographic system, and the general molecular structural features of the crystal.

The index of refraction is one of the most important physical properties used to establish the identity of the unknown crystal. Since TNT is a doubly refracting material, it is classified as an anisotropic biaxial crystal with three principle indices of refraction.

The crystallographic system of a crystal can be determined by observing the dispersion in interference figures. This will be considered in greater detail in subsequent sections.

The general structural features are deduced rather than observed by optical techniques[1]. An experienced optical investigator can rapidly deduce such features, thereby establishing clues to apply to more accurate, but time consuming research techniques. This rapidly gathered information often serves to reduce the over-all time required for a particular research problem.

A Bausch and Lomb Petrographic microscope was used for all optical observations in this project. Orthoscope features consist of a rotatable polarizer with iris diaphragm below a rotating stage and a removable

[1]Chapter VIII, Reference 10.

analyzer above the stage. Conoscope conversion for viewing interference figures consists of insertion of a Bertrand-Amici lens and a convergent substage condenser. Observation of interference figures of the TNT crystal required a 4mm objective, a 7.5X eyepiece, and a special 15X wide angled eyepiece. A 16mm objective was used for refractive index measurements.

3. Experimental Procedure.

A. Crystal Growth

The desired TNT crystals form at just below the melting point of TNT (80°C). These crystals were grown by a sublimation technique described in reference 9, and as amplified herein. Figure 1 shows the essential features of the equipment employed in this project.

TNT, Eastman Kodak, 95-99% pure 2,4,6-TNT, was placed in a glass tube (9-15mm ID) which was then evacuated and sealed under low pressure. This tube was inserted in a larger tube. Sufficient mercury was added to insure that the mercury level would be well above the TNT level of the inner tube. Short sections of glass rod were dropped around the sealed tube to provide a wedge effect, preventing vertical and lateral movement of the tube. The outer tube was then inserted in a constant temperature bath and fitted with a water cooled reflux condenser. Ethanol was added through the top of the condenser.

A Leeds and Northrup Speedomax type H recorder fitted with a series 60 duration-adjusting type control unit was used to maintain the liquid temperature bath at 85 $\pm$ 2° C. Down Corning 550 silicon oil was used as the bath fluid to avoid the problem of evaporation encountered with water at this temperature.

The mercury, acting as an 85° degree heat sink, maintained the TNT in the liquid form, and the ethanol above its boiling point (78° C.). Refluxed ethanol provided a temperature differential maintaining the top of the sealed tube slightly below the melting point of TNT; hence TNT

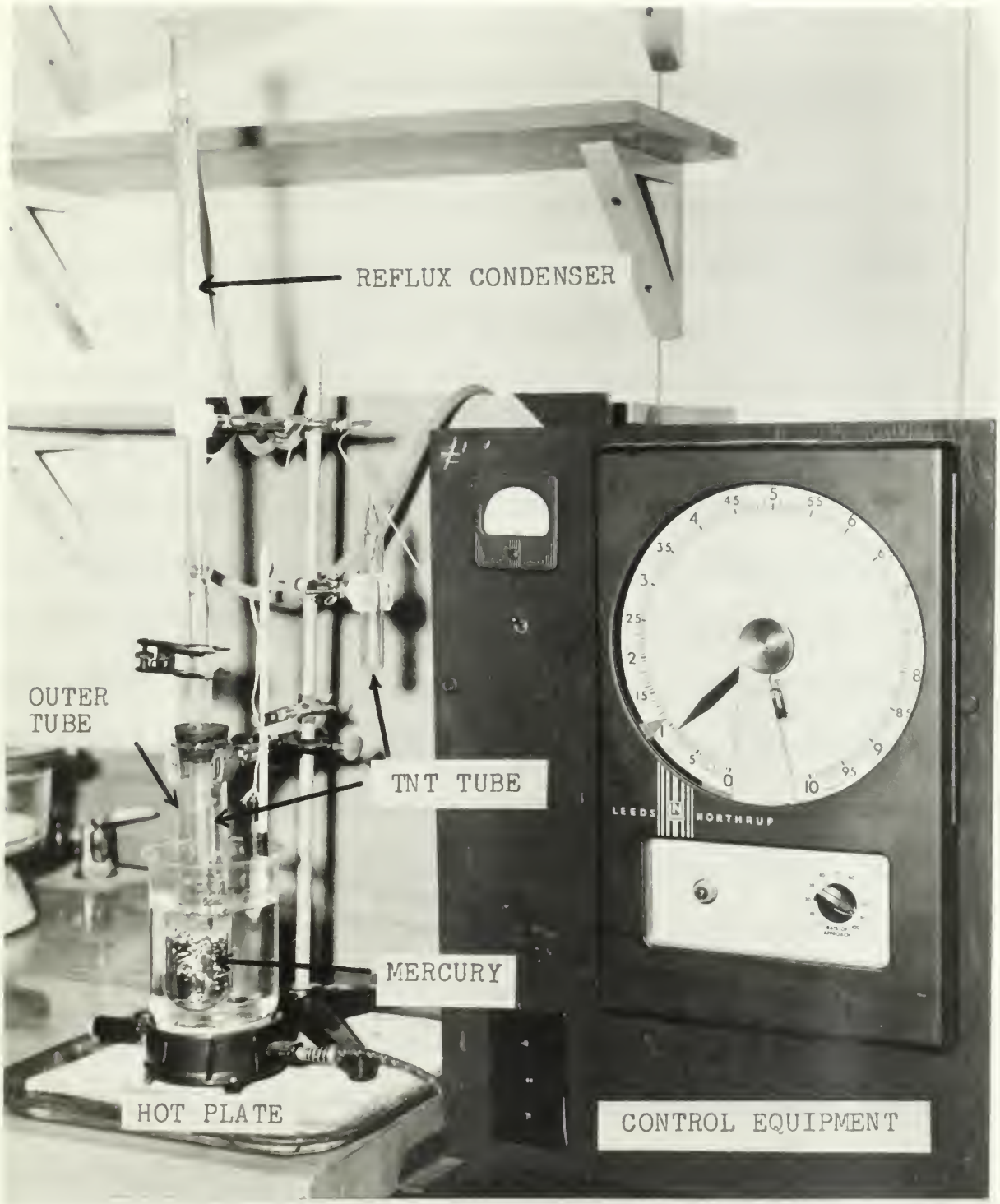



Figure 1. Crystal Growth Equipment

vapors condensed on the tube in this area forming crystals of the desired type.

Yellow, transparent, tabular crystals were obtained by the above procedure. The maximum size observed from a 14 day run were about 2mm wide by 5mm long, and approximately 0.1mm thick.

Consistently satisfactory crystals were obtained on repeated runs. The most critical parameter encountered was the pressure of the sealed tube. Reference 11 lists the generally accepted value of the vapor pressure of liquid TNT at 85° C. as 53 microns. This pressure was easily obtained with a conventional Welch DuoSeal Vacuum floor pump. All runs except one with this magnitude of pressure resulted in no crystals after a fourteen day run. On the one successful run, large crystals formed slightly above the mercury level. It was assumed that the tube had a lower pressure. A high vacuum system with an Eimac HV Diffusion Pump was used to evacuate subsequent tubes. Pressures were determined by an ion gauge. Properly sealed tubes with measured pressures of .034 microns or less resulted in formation of tiny crystals at the top of the tube within several hours after commencing a run. Within one week, crystals had grown to a sufficient size for optical work.

Best results were obtained when the refluxing ethanol was not permitted to drop onto the top of the sealed tube. This was arranged by supporting the tube vertically with short sections of glass rods and flaring the outlet of the condenser. Maintaining the temperature bath near 85° C. provided a sufficient reflux rate to establish the desired temperature

differential.

B. Optical Observations and Measurements.

Crystals were removed from the glass tube under a Bausch and Lomb binocular microscope. They were found to be quite fragile and easily shattered. With care, however, it was possible to remove any crystal desired for observation. Loose crystals were strongly attracted to a statically charged glass rod or needle, facilitating their removal from the tube.

(1) Plane Polarized Light.

Observations under plane polarized light confirmed the tabular crystal habit observed under the binocular microscope. Whole crystals tended to grow in rectangular form, indicative of slow growth by the sublimation technique. Very few needles, a characteristic of rapid growth from a solution, were observed. The width of the crystal varied considerably, but was always less than the length. It was later determined that the length was the direction of the Y axis of the biaxial indicatrix. Selective absorption of light, or pleochlorism, was very slight. On rotation of the stage, the deepest yellow color appeared with the indicatrix Z axis parallel to the direction of vibration of the polarizer, and a whitish yellow color with the Y axis so oriented. High magnification (338X) revealed numerous transparent inclusions within the crystal, and many irregular but parallel ridges along the surfaces. The former is indicative of impurities and/or entrapped gases or liquids during growth. The ridging can also be attributed to growth conditions. Fracture

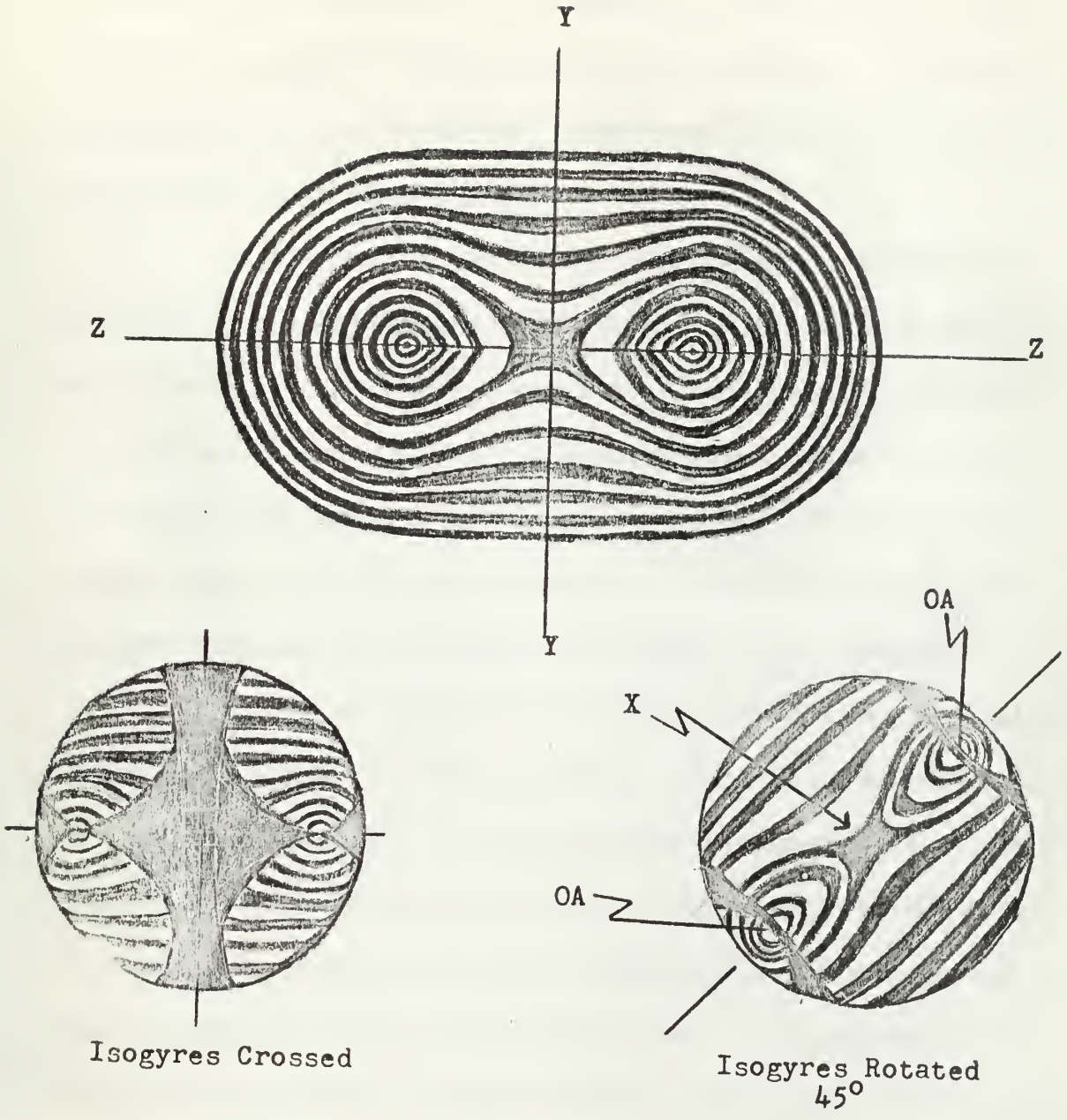
resulted in rough inclined or wedge shaped surfaces through the thickness dimension of the crystal.

(2) Crossed Polarized Light.

Observations with white light under the orthoscope demonstrated parallel extinction at ninety degree positions, a characteristic of anisotropic materials. Interference colors in non-extinction positions were present in various shades of blues and reds. Fractured inclined surfaces and the thin crystals were highly colored in blues, violets, and reds, the color lines following the parallel ridging phenomena. The thicker crystals showed hues of off-yellow, or pale pink, uniform over the entire surface area. No evidence of twinning was observed.

(3) Convergent Polarized Light.

Conoscope observations resulted in classifying the crystal as biaxial negative. The only interference figure obtained was the acute bisectrix orientation illustrated in figure 2. This was due to the thinness of the crystal plates and the extremely short working distance (0.34mm) of the conoscope with a 4mm objective. Attempts to stand the crystal on edge were futile. Crushing the crystal resulted in non-useable fragments for viewing interference figures or no change in optical orientation. The optical sign determined with a 1/4 wave length mica plate was negative. Knowledge of the optic sign permitted relating the interference figure to the biaxial indicatrix, and hence located the principle indices of refraction. As shown in figure 2, the indicatrix X axes was parallel to the tube axis of the microscope, the Z axis contained the




X Axis - Acute Bisectrix
Z Axis - Obtuse Bisectrix
Y Axis - Optic Normal
Z-Z - Trace of Optic Plane
OA - Emergence Points of Optic Axes

Figure 2. Acute Bisectrix Interference Figures. (monochromatic light)

points of emergence of the optic axis, and the Y axis was perpendicular to the Z axis through the center of the figure. Since the axes of the indicatrix represent the direction of the principle indices of refraction, this crystal orientation yielded $N_z$, the greatest index of refraction and $N_y$ the intermediate index of refraction.

Observations of dispersion phenomena in white light indicated orthorhombic dispersion (variation of the optic angle with wave length) with a tendency toward horizontal dispersion (rotation of the optic plane with wave length). In all crystals, points of emergence of the optic axes were clearly defined, and revealed colors from left to right of violet, red, red, violet (isogyres in crossed position). Thus dispersion of the crystal is greater for red light than for violet light.

The majority of crystals were too thick to permit detection of the subtle changes in coloring of the isochromatic curves. As many as sixteen isochromatic curves were present in these crystals, and appeared as solid bands of pastel shades. Isogyres were very black and broad, masking fringing phenomena. Observations with thin crystals, however, showed a slight asymmetry of colors with respect to the Z or long axis of the figure. This was noticeable particularly with the isogyres rotated to a forty-five degree position. With isogyres crossed, the optic axes emergence points for violet light were displaced slightly above those for red, indicating that rotation of the optic plane about the obtuse bisectrix differed for light of violet and red wave lengths. As with the thicker crystals, isogyres were broad and black, masking fringing effects.

(4) Index of Refraction Measurements.

The Becke line method with central illumination was used to compare the principle indices of refraction of the crystal with that of a certified liquid. Measurements were made under a sodium D light provided by a General Electric Sodium Laboratory Arc. Fresh certified Cargille index of refraction liquids, series A, B, and M, were used for all determinations. These liquids were calibrated to an accuracy of $\pm$ 0.0002 for the A and B series and $\pm$ 0.005 for the M series. Since the liquids were available in increments of .002 for series A and B, and .005 for series M, the expected precision conforms to these values.

A preliminary appraisal of the order of magnitude of the indices was made with the crystals mounted in Shillaber's immersion oil ($N_D$ 1.515). Observations indicated a very high relief with an approximate index difference of 0.2. This finding directed further efforts to liquids in the 1.7 and 1.3 regions.

For the $N_z$ and $N_y$ determinations, the acute bisectrix interference figure was oriented with the Z and Y axes parallel to the plane of vibration of the polarizer respectively. This permitted single crystal measurements. Results corrected to 25°C. were: $N_z$ 1.725 and $N_y$ 1.671. Index liquids in the range of 1.640 to 1.670 dissolved the crystal. Sufficient time was available, however, to insure accurate determination before the crystal commenced to dissolve.

As previously mentioned, an optical interference figure presenting an X indicatrix axis perpendicular to the field of view was not

available. Under such circumstances it is common practice to crush crystals and subject a large number of fragments to liquid comparisons. On rotation of the stage under plane polarized light, the crystals whose index matches that of the liquid will disappear at the extinction positions and be prominent at all other positions. This procedure is repeated over a wide range of index liquids. Since $N_x$ will be the least index of refraction, the smallest index number obtained is accepted as the correct value. Such a procedure is quite reasonable, since from a large number of fragments, all possible orientations will be present, even though fragments are imperfect and too small to show interference figures. The above procedure yielded a least index of refraction, $N_x$, of 1.544 corrected to $25^{\circ}C$..

(5) Real and Apparent Optic Angle.

The real optic angle is a property of the crystal, and a function of the wave length of light. It is related geometrically to the principle indices of refraction, from which it can be calculated[1]. The computed optic angle of the crystal under sodium D light was determined to be $61.92^{\circ}$. The apparent optic angle is caused by the refraction of light in air as it leaves the points of emergence of the optic axes; hence, as viewed in the conoscope, these points appear farther apart than if no refraction took place. This angle is simply related to the real optical angle and $N_y$[1]. Its calculated value was $118.58^{\circ}$.

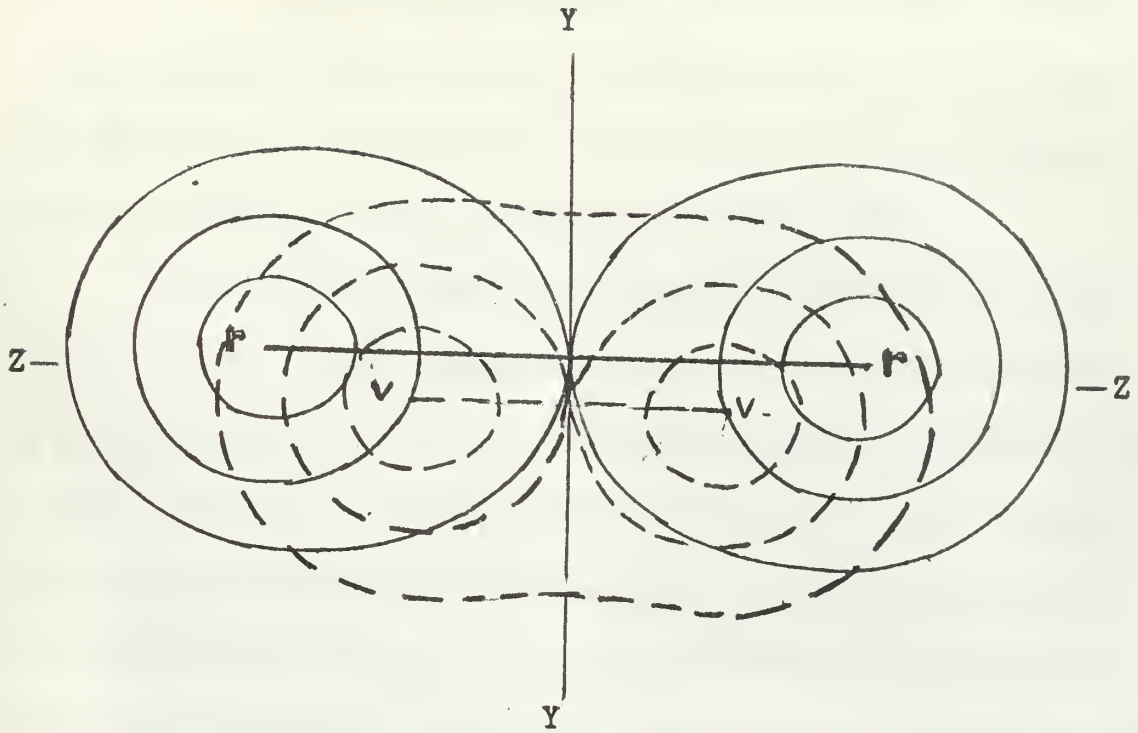
[1]Reference 11, pages 145 and 185.

4. Conclusions and Results.

A. Crystallographic Relations.

Thin plates of TNT indicated a slight tendency toward horizontal dispersion. This is characteristic only of crystals belonging to the monoclinic system. The crystallographic b axis is parallel to the Z axis of the biaxial indicatrix, and serves as the axis of rotation of the optic plane. Rotation of this plane is maximum on opposite sides of the b (hence Z) axis for the least (violet) and the greatest (red) wave lengths of the visible spectrum. Figure 3 shows the reason for asymmetry of colors on either side of the Z axis. The line r-r indicates the trace of the rotated optic plane for red light, and the line v-v the trace of the rotated optic plane for violet light. Isochromatic curves for these wave lengths are similarly displaced. This overlapping results in color curves above the Z axis being stronger in the wave lengths for red than for violet, and visa versa below the axis.

Light passing through a crystal is transmitted by the structures occupying positions at or neat the lattice sites of the crystal; hence anisotropy in the transmission of light must conform rigidly to the crystal symmetry. The biaxial indicatrix must possess the same symmetry, since it represents the variations in the indices of refraction in different directions throughout the crystal. In the monoclinic crystal, the a and c axes lie at some angle, beta, less than ninety degrees, but each is perpendicular to the b axis. The b axis is the crystal axis of two-fold symmetry, and is parallel to the Z axis of the indicatrix; thus the mutually perpen-



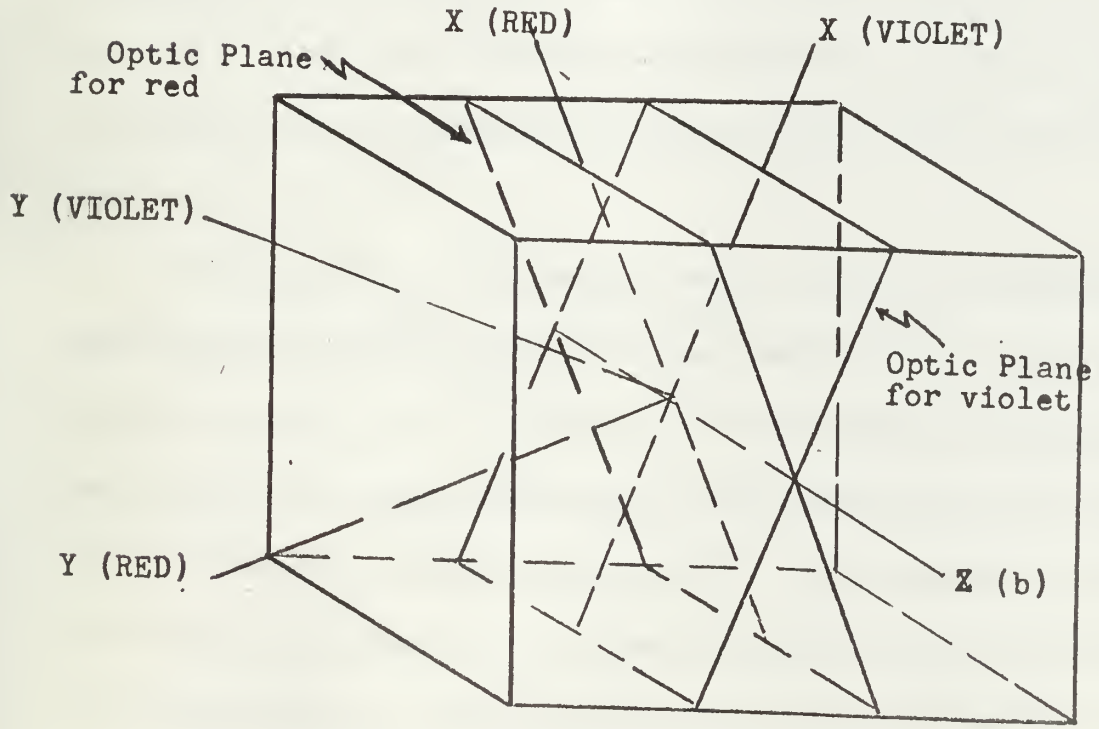




Figure 3. Horizontal Dispersion.

dicular X and Y axes will lie in the a-c plane of the crystal. As illustrated in figure 3, the X and Y axes are free to rotate in the a-c plane and about the Z axis in response to the changes in the wave lengths of light, remaining, of course, perpendicular to each other.

On the other hand, the crystallographic axes of the orthorhombic crystals are all mutually perpendicular. If the b axis lies parallel to the Z axis of the indicatrix, the Z and Y axes always must parallel the crystal a and c axes. Since the crystal axes are in a fixed orientation, then too the indicatrix axes are fixed. Light of various wave lengths cannot rotate the optic plane. Such rotation could only imply that the crystal too had rotated. Dispersion in orthorhombic crystals is limited to variations of the optic angle only, the latter assuming various values depending on the wave length of light. In figure 3, the points of emergence of the optic axes for red and violet light would all fall on the Z axis line, resulting in symmetry of the color curves above and below this line.

It is interesting to note that the angle, beta, of the monoclinic forms determined from X-ray analysis (Reference 3,4,7,9) varied as much as 30' either side of $90^{o}$. Ito (Reference 7) considered 30 minutes to be within the limits of experimental error, and reported the crystal as monoclinic on the basis of other X-ray evidence. The appearance of only a weak horizontal dispersion in the optical analysis, then, is not surprising, and substantiates the slight departure of the beta angle from $90^{o}$. Furthermore, such a small departure from the orthorhombic symmetry explains the

masking of the horizontal dispersion and fringing in the thicker crystals.

B. Imperfections.

As mentioned in the previous section, light passing through a crystal is transmitted by the ions, atoms, or molecules present at or near the lattice sites. Imperfections such as vacancies, interstitial, and substutitional impurities might be expected to modify any diffraction effect present. Since the optical interference figures are the result of light passing through a transparent crystal, any irregularities in the crystals would modify these figures. Of the fifty or more interference figures observed, no striking irregularities in isochromatic curves were detected. Additionally, observations in crossed-polarized light indicated no evidence of surface twinning. It is concluded, therefore, that imperfections, if present, are on the submicroscopic level, and techniques other than those of conventional optical crystallography are required to detect them.

C. Optical Properties.

The optical properties reported below for crystals prepared by sublimation were compared with the optical properties of crystals prepared from solution reported in reference 6. The refractive indices and the optical character agreed with the earlier data, but the sublimed crystals appeared from dispersion phenomena to be monoclinic, whereas the crystals formed from solution were reported as orthrhombic. Additionally, the order of dispersion for red and violet light was reversed for the sublimed crystal. The agreement in refractive indices is not surprising in

view of the suspected small departure of the sublimed crystals from orthorhombic symmetry. Crystals prepared from a solution of ethanol at 60°C. were observed to have the same order of dispersion as the sublimed crystals.

The optical properties of the 2,4,6-Trinitrotoluene crystal formed at 78° C. by the sublimation technique are reported as follows:

(1) Refractive Indices, corrected to 25°C., Sodium D line:

$N_x$ $1.544 \pm 0.002$

$N_y$ $1.671 \pm 0.002$

$N_z$ $1.725 \pm 0.005$

(2) Optical Character

Biaxial
Negative Sign of Double Refraction
Optic Angle (Calculated)

$2V = 61.92°$
$2E = 118.58°$

Dispersion: red greater than violet

(3) Crystallographic System:

Monoclinic

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